RDHETA 90-200-2158 NOVEMBER 1991 HAWAII STATE HEALTH DEPARTMENT NIOSH INVESTIGATORS: Greg Kullman, CIH William Jones, PhD, CIH Ronnie Cornwell, CIH John Parker, M.D.

I. SUMMARY

On March 7, 1990, The National Institute for Occupational Safety and Health (NIOSH) received a technical assistance request from the Hawaii State Health Department. The health department requested assistance in characterizing air contaminants formed when lava flow from Hawaii's Kilauea volcano vaporizes sea water. The potential for both public and occupational exposures to the lava and sea water emissions (LAZE) created health concerns. On March 13-19, 1990, NIOSH investigators conducted an environmental survey to characterize air contaminants formed by the lava and sea water. Air samples were collected for respirable dust, respirable crystalline silica and other mineral compounds, fibers, trace metals, acids, and organic and inorganic gases.

Difficult terrain, active lava flows, and varying wind patterns influenced sampling activities. Air samples were collected during four days of sampling; samples were collected within visible plumes of LAZE on March 13, 14, and 18, 1990. This LAZE contained quantifiable concentrations of hydrochloric acid (HCl) and hydrofluoric acid (HF); HCl was predominate. HCl and HF concentrations were highest in dense plumes of LAZE within approximately 12 yards of the sea. The HCl concentrations at this sampling location averaged 7.1 parts per million parts air (ppm) exceeding the occupational exposure criteria of the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute for Occupational Safety and Health (NIOSH): 5 ppm. HF concentrations were <1 ppm, below existing occupational exposure standards; although, HF exposures would produce additive effects in combination with HCl. HCl and HF concentrations decreased with distance from the source and, at distances of approximately 400 yards or greater, HCl concentrations were less than 1 ppm and HF concentrations were below detectable limits.

Sulfur dioxide $(\mathrm{SO_2})$ was detected in one of four short-term indicator tube samples at approximately 1.5 ppm demonstrating the potential for intermittent $\mathrm{SO_2}$ exposure near areas of volcanic activity and active lava flow. Short-term indicator tubes collected in the LAZE plume were below detectable limits for other gases including: ammonia, carbon disulfide, carbon monoxide, chlorine, hydrofluoric acid, hydrogen sulfide, nitrogen dioxide, and sulfuric acid. The LAZE did not contain detectable concentrations of organic gases.

Airborne particulates in the LAZE plume were comprised largely of chloride salts (predominantly sodium chloride). Crystalline silica concentrations from airborne respirable dust samples were below detectable limits, < approximately $0.03~{\rm mg/m^3}$. Airborne fibers were detected at quantifiable levels in one of 11 samples at a concentration of 0.16 fibers per cubic centimeter (f/cc). These fibers were comprised largely of a hydrated calcium sulfate similar to the mineral gypsum. Glass fibers were also detected in some air samples. These

fiber concentrations did not exceed the occupational exposure criteria of OSHA, ACGIH, or NIOSH for gypsum or fibrous glass dust.

Based on these sampling results, individuals should avoid exposure to concentrated plumes of LAZE near its origin to prevent overexposure to inorganic acids, specifically HCl. Individuals with cardiopulmonary conditions may be at increased risk and

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KEYWORDS: SIC9999, Volcano, Lava, LAZE, Hydrochloric Acid, Hydrofluoric Acid, Sulfur Dioxide, Fibrous Glass, Gypsum.

II. INTRODUCTION

On March 7, 1990, The National Institute for Occupational Safety and Health (NIOSH) received a technical assistance request from the Hawaii State Health Department. The health department requested assistance in characterizing air contaminants formed when lava flow from Hawaii's Kilauea volcano vaporizes sea water. This interaction of lava with sea water produces large clouds of visible mist (lava and sea emissions - LAZE¹). Island wind patterns (Kona winds) occasionally move this LAZE towards populated areas in the adjacent village of Kalapana² and into the Hawaii Volcanos National Park. The potential for both public and occupational exposure to the LAZE created health concerns. On March 13-19, 1990, NIOSH scientists from the Division of Respiratory Disease Studies conducted an environmental survey to characterize the contaminants formed by the interaction of lava and sea water. To address immediate health concerns, sampling results were communicated to the health department by telephone as individual laboratory analyses were completed. On June 7, 1990, an interim environmental report was completed.

III. BACKGROUND

The Hawaiian Archipelago stretches for 1500 miles across the north central Pacific Ocean. The eight major islands of the archipelago are: Niihau, Kauai, Oahu, Molokai, Lanai, Kahoolawe, Maui, and Hawaii (figure 1). These islands are the tops of a large mountain range built up over 15,000 feet from the ocean floor by numerous volcanic eruptions and lava flows. The volcanic activity that formed these islands is believed to have started at the northwest end of the Hawaiian Archipelago and shifted progressively to the southeastern island, Hawaii. Theory suggests that these volcanos (and islands) are formed as the earth's pacific plate moves across a fixed hot spot (or hole) in the earth's mantle during the northwest plate drift (1,2,3).

Hawaii, the southern most island of the Hawaiian archipelago, is the youngest island and has the most volcanic activity. Known as the "Big Island," Hawaii has an area of 4,030 square miles (approximately the size of Connecticut). The island was formed by lava flows from five volcanos: Kohala, Hualalai, Mauna Kea, Mauna Loa, and Kilauea (figure 2). Mauna Loa and Kilauea, the two southernmost volcanos, are considered active and among the most active volcanos in the world. Kilauea is presently the most active Hawaiian volcano. In January 1983, Kilauea began the longest sustained eruption of any Hawaiian volcano in recorded time and this eruption is still in progress (1,2).

Molten rock from volcanic eruptions is a complex solution of silicates and oxides associated with water vapor and possibly other gases. Lavas can vary in composition.

Hawaiian lavas have a lower silica content and are rich in iron, magnesium, and calcium as indicated below: $^{(1)}$

¹ The term LAZE was used by Hawaii Civil Defense and Hawaii Health Department personnel to describe the mist formed by the interaction of lava and sea water.

² The village of Kalapana was destroyed by lava flows during the summer/fall of 1990.

³ A volcano is an opening in the earth's crust from which molten rock and gases are released.

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AVERAGE CHEMICAL COMPOSITION OF LAVA

Oxide	Percenta	ages
	Hawaiian	Mt.
	Volcanoes	St. Helens Volcano
		Washington State, USA
Silicon Dioxide	48.4	63.5
Aluminum Oxide	13.2	17.6
Iron Oxides	11.2	4.2
Magnesium Oxide	9.7	2.0
Calcium Oxide	10.3	5.2
Sodium Oxide	2.4	4.6
Potassium Oxide	0.6	1.3
Titanium Dioxide	2.8	0.6
Other	1.4	1.0

Olivine basalt is the most common lava from recent eruptions of Kilauea and Mauna Loa volcanos. Hawaiian lavas are more viscous with a lower gas content resulting in gentler, less explosive volcanic eruptions. Hawaiian volcanos erupt not only at their summits but also along rift zones which are heavily fractured zones of weakness in the volcano. Lava flows from eruptions of Hawaiian volcanos are generally of two types: Pahoehoe and Aa. Pahoehoe has a smooth, ropey or billowy surface; Aa has a very rough or jumbled surface (lava rock) but with similar chemical composition to pahoehoe lava (1-3). Pahoehoe lava flows can also occur on the surface or within lava tubes beneath the surface of lava that has cooled and crusted. In the path to lower coastal areas, these Hawaiian lava flows often destroy vegetation, roads, or villages scorching everything in their path. At the ocean, lava flows contribute to the process of island building, creating new land. The interaction of the molten lava with ocean water can be explosive and produce large clouds of ${\rm LAZE}^{(1,2)}$. These LAZE clouds move in various directions depending on prevailing wind patterns. Kona conditions, winds moving from the southeast to the northwest, can push the LAZE onto land and into the Hawaii Volcano's National Park and other populated island areas creating potential for both occupational and community exposure.

IV. METHODS

An environmental survey was done to characterize the air contaminants formed by the interaction of lava and sea water. Air samples were collected for several environmental analytes including respirable dust, respirable crystalline silica and other minerals, fibers, trace metals, acids and organic and inorganic gases. Table 1 describes the sampling methods used during the survey.

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TABLE 1 ENVIRONMENTAL SAMPLING METHODS RDHETA 90-200

Analyte	Sampler	Media	Air Sampling Rate	Sampling Time	Sample Analyses
Respirable Dust and Crystalline Silica	Respirable Cyclone	Polyvinyl Chloride Filter (37 mm)	1.7 liters per minute (lpm)	2-8 hours	 Gravimetric x-ray Diffraction NIOSH Method 7500⁽⁴⁾
Metals/ Elements	Total Dust Cassette	Mixed Cellulose Ester Filter (37	2.0 lpm mm)	2-8 hours	1. Inductively Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES) NIOSH Method 7300 (4)
Minerals/ Fibers	Total Dust Cassette	Mixed Cellulose Ester or Poly- carbonate Filter	2.0 lpm	1/4-2 hours	 Transmission Electron Microscopy - NIOSH Method 7402⁽⁴⁾ Polarized Light Microscopy PLM ⁽⁴⁾ Scanning Electron Microscopy
	Bulk Materials Container				 PLM Scanning Eletron Microscopy
Hydrocarbon Vapors	Solid Sorbet Tube	Charcoal and Silica Gel	0.05 lpm 0.2 lpm	2-8 hours	1. Gas Chromatography (4)
Inorganic Acids	Solid Sorbet Tube	Silica Gel	0.2 lpm	2-8 hours	1. ION Chromatography- NIOSH Method 7903 ⁽⁴⁾
		TABLE 1 ENV	TRONMENTAL SAM RDHETA 90-200		
Analyte	Sampler	Media	Air Sampling	Sampling	Sample

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			Rate	Time	Analyses
Inorganic Acids	Midget Impinger	Sodium Hydroxide Solution	1.0 lpm	2-8 hours	1. ION Chromatography ¹
	Midget Impinger	Deionized Water	1.0 lpm	2-8 hours	 ION Chromatography¹ Metals ICP-AES (4)
	Glass Condenser			2 hours	 ION Chromatography (4) PH Measurements
Gases (inorganic) Ammonia Carbon Dioxide Carbon Disulfide Carbon Monoxide Chlorine Hydrochloric Acid Hydrofluoric Acid Hydrogen Sulfide Nitrogen Dioxide Sulfuric Acid Sulfur Dioxide		Tubes		5 minutes	1. Colormetric - Length of Stain in sample tube proportional to air concentration of contaminant. A direct measure. (5)

Sampling analytical methods for inorganic acids were selected based on conversations with chemists from NIOSH's Division of Physical Sciences and Engineering and the United States Environmental Protection Agency.

Area sampling stations were used to measure the air contaminants formed by the lava and sea water. The following sampling locations were selected based on conversation with Hawaii State Health Department and Hawaii Civil Defense Personnel (Figure 3):

- 1. <u>Beach areas</u> sampling stations positioned in the visible clouds of LAZE at distances from 10 to 400 yards from the lava/sea water source.
- 2. <u>Roadblock</u> sampling station positioned on Highway 130 roadblock west of Kalapana, Hawaii. This station was positioned at one of the closest points of public access to the LAZE formation.
- 3. <u>Kalapana, Hawaii</u> 2 sampling stations
 - A. <u>Papaya Plant</u> Near the intersection of highway 130 and highway 137.
 - B. <u>Village Residence</u> On highway 130 approximately 1/2 mile east of the tourist roadblock.
- 4. <u>Background</u> sampling station located at the fire station in Keaau, Hawaii near the intersection of highways 130 and 11.
- 5. <u>Hawaii Volcano's National Park</u> Two sampling stations positioned approximately 2.5 and 4.5 miles downwind from the LAZE origin.

The sampling design called for the collection of air samples during Kona wind conditions when the LAZE was directed into Kalapana, HI and surrounding areas. (Wind patterns during the survey did not direct the LAZE into Kalapana; although, on 3 of 7 scheduled survey dates wind carried mists directly over land enabling us to collect both concentrated and diluted plume samples). Samples were collected during four days - March 13-15 and March 18, 1990.

V. <u>EVALUATION CRITERIA</u>

Evaluation criteria are guidelines commonly used by NIOSH investigators to assess the potential health effects of occupational exposures to substances and conditions found in the work environment. These criteria consist of exposure levels for substances and conditions to which most workers can be exposed day after day for a working lifetime without adverse health effects. Because of variation in individual susceptibility, a small percentage of workers may experience health problems or discomfort at exposure levels below these criteria. Consequently, it is important to understand that these evaluation criteria are guidelines for occupational exposures, not absolute limits between safe and dangerous levels of exposure.

Several sources of evaluation criteria exist and are commonly used by NIOSH investigators to assess occupational exposures. These include:

- 1. The U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) permissible exposure limits (PEL's); $^{(6)}$
- 2. The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit (Exposure) Values (TLV's); (7)
- 3. NIOSH recommended exposure limits (REL's). (8)

¹ These sampling stations were located at points used by the Hawaii State

Health Department for airborne particulate sampling.

These criteria have been derived from industrial experience, from human and animal studies, and when possible, from a combination of the three. Due to differences in scientific interpretation of these data, there is some variability in exposure recommendations for certain substances. Additionally, OSHA considers economic feasibility in establishing occupational exposure standards; NIOSH and ACGIH do not consider economic feasibility in development of their criteria.

The exposure criteria described in this report are: Time-weighted average (TWA) exposure recommendations averaged over the full work shift; short-term exposure limit (STEL) recommendations for a brief (10-15 minute) exposure period; and ceiling levels (C) not to be exceeded for any amount of time. These exposure criteria and standards are commonly reported as parts contaminant per million parts air (ppm), or milligrams of contaminant per cubic meter of air (mg/m 3). Occupational criteria for the air contaminants measured during this study are presented in Table 2. (6-8)

In addition to the occupational exposure criteria/standards of NIOSH, ACGIH, and OSHA, the Environmental Protection Agency (EPA) promulgates national primary and secondary ambient air quality standards for some of the contaminants detected during this survey; these standards are designed to protect public health and welfare and would be more appropriate than occupational criteria to evaluate non-occupational, community exposure risks. The national primary and secondary ambient air quality standards for particulates are $0.15~{\rm mg/m^3}$ as a $24-{\rm hour}$ average concentration and $0.05~{\rm mg/m^3}$ as an annual arithmetic mean. (9) The national primary and secondary ambient air quality standards for sulfur dioxide include: (9)

Primary - 0.03 ppm - Annual Arithmetic Mean.
Standard - 0.14 ppm - Minimum 24-hour concentration not to be exceeded more than once a year.

Secondary - 0.5 ppm - 3-hour concentration not to be exceeded more Standard than once a year.

There are no national ambient air quality standards for hydrochloric acid, hydrofluoric acid, or other contaminants measured during the evaluation. Other community health exposure standards suitable to gauge exposure risks for those substances measured during this evaluation were not identified.

TABLE 2 OCCUPATIONAL EXPOSURE CRITERIA RDHETA 90-200

CONTAMINANT (PEL)	NIOSH (REL)	ACGIH (TLV)	<u>OSHA</u>
Calcium Carbon Dioxide ppm (TWA)	No REL 10,000 ppm (TWA)	No TLV 5,000 ppm (TWA)	No PEL 10,000
ppm (STEL)	30,000 ppm (STEL)	30,000 ppm (STEL)	30,000
Copper mg/m³ (TWA)	$1 \text{ mg/m}^3 \text{ (TWA)}$	$1 \text{ mg/m}^3 \text{ (TWA)}$	1
Fibrous Glass	5 mg/m ³ (TWA)	$10 \text{ mg/m}^3 \text{ (TWA)}$	No PEL
Development	3 f/cc (TWA) ²		
Calcium Sulfate (Gypsum) Total Dust mg/m³ (TWA)	10 mg/m^3	10 mg/m³ (TWA)	15
Respirable Dust ¹ mg/m ³ (TWA)	5 mg/m ³	No TLV	5
Hydrochloric Acid ¹ (C)	5 ppm (C)	5 ppm (C)	5 ppm
Hydrofluoric Acid	3 ppm (TWA)		3 ppm
(STEL)	6 ppm (C)	3 ppm (C)	6 ppm
Iron Dust ¹ mg/m³ (TWA)	5 mg/m ³ (TWA)	5 mg/m ³ (TWA)	10
Magnesium	No REL	No TLV	No PEL
Respirable Dust mg/m³ (TWA) (Particulates Not Otherwise Regulated)	No REL	No TLV	5
Sodium (Sodium Chloride)	No REL	No TLV	No PEL
Sulfur Dioxide (TWA)	0.5 ppm (TWA)	2 ppm (TWA)	2 ppm
(STEL)		5 ppm (STEL)	5 ppm

TWA - Time-weighted Average, STEL - Short-term Exposure Limit, C - Ceiling Exposure Limit,

PPM - Parts Per Million Parts Air by Volume, mg/m³ - Milligram Per Cubic Meter of Air, f/cc - Fibers Per Cubic Centimeter of Air

 $^{{\}bf 1}$ - Denotes substances for which the NIOSH recommendation is derived from NIOSH testimony provided to OSHA.

^{2 -} For fibers \leq 3.5 um in diameter and \geq 10 um in length.

Summary of Toxicology

The following information describes the possible toxicological effects for workers exposed to the substances monitored during this survey. These effects are described so individuals will be familiar with the symptoms and consequences of overexposure. The effects depend on factors including contaminant concentration, length of exposure, activity or workload, individual susceptibility, and synergistic or additive effects of combined exposures.

Hydrogen Chloride:

Hydrogen chloride (HCl) is a colorless gas with a pungent irritating odor. HCl dissolves in water to form the aqueous solution hydrochloric acid, which can contain up to 38 percent HCl. $^{(9,10)}$ HCl can affect the body if it is inhaled, ingested, or if it comes in contact with the eyes or skin. When HCl is inhaled, it can cause irritation of the respiratory tract with burning, choking, and coughing. Breathing difficulties may occur which may be delayed in onset. HCl can cause eye irritation, severe burns, and permanent damage with loss of sight. Skin contact with HCl can cause irritation and severe burns. Repeated or prolonged exposures to HCl can cause erosion of the teeth and skin rash. $^{(10,13)}$

HCl concentration of 100 ppm or greater are considered immediately dangerous to life and health (IDLH). Henderson and Haggard report that men exposed to 50-100 ppm HCl for 1 hour found the exposure barely tolerable; short-term HCl exposure of 35 ppm caused throat irritation. Several studies suggest that exposures of 5 ppm or more are immediately irritating. $^{(10-12)}$ The ACGIH-TLV and OSHA-PEL for HCl is 5 ppm as a ceiling exposure level. $^{(6,7)}$ NIOSH also recommends that worker exposures to HCl be maintained below a 5 ppm ceiling. Persons with impaired pulmonary functions may be at increased risk from HCl exposure at or below existing occupational standards. $^{(10)}$

Hydrogen Fluoride:

Hydrogen Fluoride (HF) is a colorless gas at temperatures above 67 $^{\circ}F$ (the HF boiling point) and a fuming liquid at lower temperatures. When HF is dissolved in water it forms an aqueous solution, hydrofluoric acid, which can contain 60% HF. Commercially prepared liquid solution can contain 100% HF. HF can affect the body if it is inhaled, ingested, or if it comes in contact with the eyes or skin. When HF is inhaled, it can cause severe respiratory irritation, inflammation, and congestion of the lungs at higher exposures. Breathing difficulties may not occur until some hours after exposure has ended. HF can cause irritation, deep-seated burns of the eye and eye lids, and severe skin burns. HF is also a severe irritant to the nose and throat. Acute overexposures to HF can also cause kidney and liver damage.

Fatalities are reported among workers exposed to concentrated HF solution during spills; death was from pulmonary edema occurring 2 to 3 hours after exposure. An HF concentration of 300 ppm was fatal to rabbits and guinea pigs exposed for 2 hours. In humans, 120 ppm was the highest concentration that could be tolerated for 1 minute due to the onset of conjunctual and respiratory irritation. HF at concentration of 30 ppm or greater is considered IDLH. Repeated exposure to HF at 17 ppm caused lung, liver, and kidney damage to laboratory animals. Repeated human exposure to 2 ppm HF for 6 hours daily caused stinging of the eyes skin and face with nasal irritation. Burns do not manifest immediately on skin contact with HF solutions of less than 50% HF; burns from anhydrous HF solution exceeding 50% are felt in a matter of minutes and can cause necrosis of deep tissue and damage to the bone.

The OSHA- PEL for HF is 3 ppm as a TWA with a 6 ppm STEL. $^{(6)}$ ACGIH recommends a ceiling TLV of 3 ppm for HF to guard against primary irritant effects and minimize fluorosis. $^{(7)}$ The NIOSH-REL for HF is 3 ppm as a TWA and 6 ppm as an exposure ceiling. This REL is based on irritation of the eyes, skin, and respiratory tract, and potential increase in bone density due to skeletal fluorosis.

Fibrous Glass:

Glass fibers are elongated particles with an aspect ratio (length divided by width) of 3 or longer. These fibers are generally comprised of borosilicate or calico-aluminum silica glass. An important physical characteristic of glass fibers is that, in contrast to asbestos, they cannot fracture longitudinally into finer fibrils and are subject to transverse fracture to fibers of shorter length with the original diameter maintained. (16,17) The diameter of glass fibers is a significant characteristic determining physical properties, commercial applications, and behavior in an air stream. Glass fibers with diameter less than 3.5 um can penetrate to the gas exchange region of the lung with maximum alveolar deposition in 2 um diameter fibers. Glass fibers with diameters larger then 3.5 um are primarily deposited in the nasopharynx, trachea, and bronchi. (18)

Fibrous glass exposure can cause a mechanical transitory skin irritation with symptoms of itching or prickling especially in skin folds. Exposure to glass fibers can also be irritating to the eyes and respiratory tract. (11,15-18) In different dimensions, fibrous glass can cause varying biological effects. Large diameter fibers (>3.5 um) have been found to cause skin, eye, and upper respiratory tract irritation; a relatively low frequency of fibrotic changes; and a very slight indication of nonmalignant respiratory disease. Smaller diameter fibrous glass (<3.5 um) is capable of penetrating to gas exchange regions of the lung; experimental studies have demonstrated fibrogenic and carcinogenic effects with long (>10 um length) and thin (<1 um diameter) fibers. However, these studies were performed by implanting fibrous glass in the pleural or peritoneal cavities and biological effects from this exposure route are difficult to interpret since they cannot be extrapolated to conditions of human exposure. $^{(15,18)}$ The ACGIH- TLV for fibrous glass is 10 mg/m^3 as a TWA and based on nuisance dust criteria. Although, the health effects of fibrous glass is currently under study by ACGIH. The OSHA standard for fibrous glass is in development at the writing of this report. (6) The NIOSH REL for fibrous glass is 5 mg/m³ as a TWA with a 3 fiber/cc limit on fibers with diameters less than or equal to 3.5 um and lengths greater than or equal to 10 um. This REL is based on increased health concern of fibrosis and respiratory tract irritation in longer, small diameter fibers.

Gypsum:

Gypsum or hydrated calcium sulfate (CaSO $_4.2H_2O$) is rarely found pure and deposits may contain quartz, pyrites, carbonates, and bituminous materials. Gypsum occurs in nature in five varieties: gypsum rock; gypsite (an impure earthy form); alabaster (a massive, fine-grained variety); satin spas (a fibrous, silky form); and selenite (transparent crystals) $^{(12,17)}$

Gypsum dust has an irritant action on the mucous membrane of the respiratory tract and there have been reports of conjunctivitis, chronic rhinitis, laryngitis, pharyngitis, impaired sense of smell and taste, and nose bleeds among exposed workers. $^{(17,18)}$ Some studies suggest that prolonged exposure to gypsum dust is associated with pneumoconiosis and decrements in pulmonary function. $^{(19)}$ Although, other sources state that animal studies using pure gypsum failed to produce lung fibrosis. $^{(20)}$

The ACGIH considers gypsum to be a nuisance particulate (of a low order of toxicity) which causes no lung disease. The ACGIH- TLV for gypsum is 10 mg/m 3 as a TWA. $^{(7,12)}$ The OSHA-PEL for total gypsum dust in air is 15 mg/m 3 as a TWA and for respirable dust 5 mg/m 3 as a TWA. $^{(6)}$ The NIOSH-REL for total gypsum dust in air is 10 mg/m 3 as a TWA and for respirable dust 5 mg/m 3 as a TWA. $^{(15)}$

Sulfur Dioxide:

Sulfur dioxide (SO_2) is a colorless, water-soluble gas formed when sulfur containing materials are burned. Sulfur dioxide is a severe irritant of the eyes, mucous membranes, and skin. Its irritant properties are due to the rapidity with which it forms sulfurous acid (H_2SO_3). This reaction can occur on the mucous membranes lining the respiratory tract causing immediate irritation and constriction of respiratory air passages. Inhalation of large amounts of SO_2 can result in death from asphyxia. SO₂ concentrations of 100

ppm or higher are considered IDLH. Exposure to concentrations of 10 to 50 ppm for 5 to 15 minutes causes irritation of the eyes, nose, and throat; coughing, choking, and in some instances broncho-constriction with increased pulmonary resistance. In a human exposure study, subjects exposed to 13 ppm SO $_2$ suffered a 73% increase in resistance to pulmonary flow; 1 ppm produced no effects. Although, there is varying sensitivity among different individuals to the broncho-constricting effects of SO $_2$. Bronchial asthma has also been attributed to acute SO $_2$ exposures. Workers repeatedly exposed to 10 ppm experienced upper respiratory tract irritation and some nose bleeds, but the symptoms did not occur at 5 ppm. $^{(10-12)}$ SO $_2$ and other ambient air pollutants can contribute to or aggravate other respiratory health problems including chronic bronchitis, emphysema, lung cancer or other nonspecific upper respiratory tract disease.

Among occupational exposure criteria, the ACGIH-TLV and OSHA-PEL for SO $_2$ are 2 ppm as a TWA and 5 ppm as a STEL. (6,8) The NIOSH-REL for SO $_2$ is 0.5 ppm as a TWA. (7,15) The EPA primary ambient air quality standards for SO $_2$ include 0.03 ppm as an annual arithmetic mean and 0.14 ppm as a minimum 2-4 hour concentration not to be exceeded more than once a year. The EPA secondary standard for SO $_2$, a 3 hour concentration not to be exceeded more than once a year, is 0.5 ppm. (9)

VI. RESULTS/DISCUSSION

The objective of this evaluation was the characterization of air contaminants formed when lava from Hawaii's Kilauea Volcano vaporizes sea water. This information was needed to address the potential exposure hazards for workers and area residents periodically exposed to the LAZE during KONA wind patterns. Kilauea, since 1983, is in the longest sustained eruption in recorded time, although, volcanic activity has been variable in term of both lava flow and flow direction. The lava flows observed during our survey were primarily tubular with some areas of active surface flows. The interaction of lava and sea water produced massive clouds of fine mist. The direction of movement and the shape of these mist plumes were largely a function of island wind patterns. On March 13, 14, and 18, 1990, winds from the south and east were sufficient to move the LAZE over land and permit the collection of air samples from the beach front sampling stations. Sampling efforts were complicated by difficult terrain and active lava flows; although we were successful in collecting samples directly in the LAZE plume at varying distances from the point of lava/sea water interaction. Island wind patterns did not direct the LAZE into the village of Kalapana during our survey; consequently, the air samples collected from the sampling stations in and around Kalapana reflect background, ambient concentrations.

To aid in the characterization of the LAZE, a 6.4 milliliter (ml) sample of condensate was collected in dense clouds of LAZE approximately 10-12 yards from its origin. This liquid had a pH of approximately 1.3 which is consistent with pH readings obtained by placing strips of pH paper directly in the clouds of mist. The condensate sample, analyzed for inorganic acids by ion chromatography, contained Hydrochloric acid (11 mg); Hydrofluoric acid (0.25 mg), and sulfate anion – SO_4 (0.8 mg) 1 . Other anions (bromide, nitrate, and phosphate) were not detected in this sample. There was insufficient volume of condensate for trace metal analysis or any additional analyses. These measurements show that the LAZE is highly acidic, with the acidity being mainly a function of HCl content. These findings are consistent with research data from the U.S. Geological Survey indicating that HCl can be formed by the steam hydrolysis of magnesium chloride salts precipitated when sea water is

 $^{^1}$ Analysis by ion chromatography and ion pair chromatography failed to give a clear separation of sulfate and perchlorate. Thus, the presence of perchloric anion can neither be confirmed nor rejected in this condensate sample. Consequently, a portion of the sulfate results may partially represent perchloric anion response. Indicator tube samples (H_2SO_4) and mineralogical analysis suggest that sulfate ion in this sample may have been present as a mineral complex similar to gypsum and not as sulfuric acid (H_2SO_4) .

evaporated to dryness by molten lava. (21,22)

Time-weighted average (TWA) air samples were collected to measure inorganic acid concentrations using several sampling methods including: Silica gel sorbent tubes, midget impingers containing NaOH, and midget impingers containing deionized, distilled water. HCl was the predominant inorganic acid in air. The average HCl concentration from the 2 impinger samples collected at each sampling location ranged from below detectable limits (ND) to 10 ppm (Table 3).

These HCl concentrations are based on total Cl anion per sample. (The ion chromatograph can not distinguish a chloride anion derived from HCl from a chloride anion from ocean salts). To estimate the chloride anion potentially consumed as ocean salt, each distilled water impinger sample was analyzed for metals commonly bound as chloride salts. Concentration adjustments for chloride anion potentially bound as salts of calcium, magnesium, or sodium may have reduced HCl concentration to an estimated 87 percent of reported concentration in impinger samples collected in concentrated LAZE plume near origin and to 36 percent of reported concentration in less dense LAZE plumes approximately 400 yards from origin. (Table 3 and Appendix A). The HCl concentrations measured using the silica gel sorbent tubes were in agreement with the impinger results. Average HCl concentrations from the two sorbent tubes collected at each area sampling station ranged from ND to 8.8 ppm (Table 4).

HCl concentrations were the highest in those sampling stations positioned directly in the LAZE plume near the point of origin. The 8 TWA samples (impingers and sorbent tubes) collected in dense mists within approximately 12 yards of a tubular LAZE source on March 14, 1990 had a mean concentration of 7.1 ppm with a standard deviation (SD) of 2.9. Four direct reading indicator tube samples collected at this same location had an average concentration of 6.4 ppm. As indicated in Figure 4, HCl concentrations declined with distance from the source. At approximately 100 yards, the average, TWA HCl concentrations from 8 samples was 0.69 ppm with a SD of 0.51. The nine direct reading indicator tubes collected at this distance had an average concentration of 0.33 ppm. Four TWA samples collected at approximately 400 yards from the LAZE source on March 18th had an average concentration of 0.39 ppm with a SD of 0.11. The three indicator tubes collected at this distance had an average concentration of 0.4 ppm. Samples collected within the LAZE plume at distances of approximately 2.5 and 4.5 miles from origin were below quantifiable limits for HCl. HCl concentration from other locations outside of the direct LAZE plume were generally below detectable limits and a reflection of ambient or background conditions.

HCl concentrations measured in the dense LAZE plume within 12 yards of the source were in excess of the occupational exposure standard enforced by OSHA, 5 ppm as a ceiling level. These area HCl concentration also exceeded NIOSH and ACGIH occupational exposure recommendations, (also 5 ppm as a ceiling exposure value).

The impinger and silica gel sorbent tubes were also analyzed for anions of other inorganic acids including bromide , fluoride, nitrate, perchloric, phosphate, and sulfate. Of these, fluoride, nitrate, perchloric¹, and sulfate were identified in some samples collected from the sampling stations within the plume. Nitric and perchloric acids were below quantifiable levels in all samples. Hydrofluoric acid (HF) was detected in 9 of 20 samples, from the beach sampling stations.

Four of the samples had quantifiable HF concentrations. The highest HF concentration 0.99 ppm was measured in a dense plume on March 14, 1990. Fluoride anion was also detected at quantifiable levels in four samples collected from sampling stations located outside of the plume. The highest concentration, 0.19 ppm HF, was collected at the roadblock sampling station. The presence of fluoride anion in these background ambient samples may be attributed to vent gas emissions from Kilauea. None of the area HF concentrations exceeded the personal exposure standards/criteria of OSHA, ACGIH, or NIOSH (3 ppm as a TWA); although HF exposures would have an additive health effect in combination with HCl exposures. (11)

Sulfate anion (SO₄) was detected in 14 of 20 samples from the beach sampling

stations with concentrations ranging to 1 mg/m^3 . It is unlikely that this anion was present as sulfuric acid (H_2SO_4) since indicator tube samples for

sulfuric acid, collected in dense LAZE mist, were below detectable limits. A more probable source of the SO_4 in these samples is a mineral, similar to gypsum ($CaSO_4.2H_2O$), that was identified in many airborne samples by transmission electron microscopy analysis.

Direct reading indicator tube samples, taken to evaluate potential presence of a number of chemical substances in the LAZE, were below detectable levels for ammonia, carbon disulfide, carbon monoxide, chlorine, hydrofluoric acid, hydrogen sulfide, nitrogen dioxide, sulfuric acid. Carbon dioxide, hydrochloric acid, and sulfur dioxide were measured at detectable levels. (Table 5) HCl concentrations were discussed in previous report section. The two carbon dioxide measurements, 400 and 450 ppm, were close to expected ambient levels. Sulfur dioxide was detected in one of four short-term samples at a concentration of 1.5 ppm. This sample was below the OSHA- PEL and ACGIH-TLV (5ppm as a STEL), but high by comparison to the NIOSH-REL, 0.5 ppm as a TWA, and demonstrates potential for periodic SO_2 exposures in areas of volcanic activity/lava flow.

Volatile organic compounds were <u>not</u> detected in any of the thirteen high volume charcoal and silica gel tube samples analyzed qualitatively. Consequently, the additional low volume samples collected during this survey were not analyzed quantitatively. This sampling was done to assess potential for volitization of carbonaceous materials on land or at sea by lava flows.

Respirable dust and crystalline silica results are presented in Table 6. Respirable dust concentrations ranged from below detectable levels (LOD = 0.01 $\,\mathrm{mg/m^3})$ to a high of 1.3 $\,\mathrm{mg/m^3}$. The 5 samples collected from beach sampling stations, within the LAZE plume, had an average concentration of 0.5 $\,\mathrm{mg/m^3}$ with a SD of 0.48. Respirable dust concentrations from other sampling stations out of the plume were below 0.03 $\,\mathrm{mg/m^3}$ and reflect ambient or background conditions. Crystalline silica (alpha-quartz, cristolite, or tridymite) was not detected in any of the samples. The limit detection for crystalline silica is 0.015 $\,\mathrm{mg/sample}$ or approximately 0.03 $\,\mathrm{mg/m^3}$ given the average volume sampled.

Table 7 presents trace metal sampling results from filter samples collected in an open face cassette. Calcium, copper, iron, magnesium, sodium, and zinc were detected in these samples. Metal concentrations were highest in the beach sampling stations positioned in the LAZE plume. Sodium and magnesium were the most abundant metals. Sodium was detected in each sample collected from the beach sampling stations at concentrations ranging from 0.03 mg/m³ to 1.0 mg/m³. Magnesium was detected in 4 of the 5 samples from this area at concentrations ranging from ND (<0.003 mg/m³) to 0.13 mg/m³. Sodium and magnesium salts comprise over 90 percent of the total ocean salts (by weight) and their presence is consistent with particulate formed from boiled/evaporated sea water. Exposures to sodium, magnesium, and the other metals identified in these samples were well below existing occupational exposure standards/criteria of OSHA, ACGIH, and NIOSH. (Table 2)

perchloric acid was identified in the silica gel sorbent tubes.

Laboratory analyses were unable to resolve the perchloric anion from the sulfate ion in the condensate and impinger samples.

The nature of the particulate formed by the interaction of lava and sea water was evaluated in several ways. By visual observation of LAZE plumes, particulate fall-out could be observed on occasion. These particles, thin sheets or flakes measuring up to approximately 10 cm in diameter, have been recently described as LIMU'O PEL or Pele's seaweed.²

They are comprised largely of amorphous silicon dioxide. (Figure 5) This material, as well as fibrous glass particles, could be observed in the crevices of lava near the ocean. The aerosolization of this amorphous glass results from the explosive interaction of lava and sea water.

Microscopic analysis of air samples collected on filter media or by suspending a microscope slide directly in the LAZE plume, showed a predominance of cubic crystals. (Figure 6) Further observation of these particles by polarized light microscopy indicated that they were isotropic which suggests NaCl. Confirmation was obtained by scanning electron microscopy with x-ray analysis.

FIGURE 1. THE HAWAIIAN ARCHIPELAGO RDHETA 90-200

NITHAU

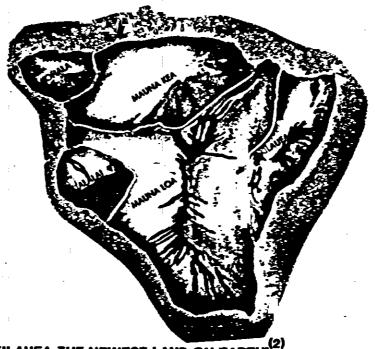
QANU

MOLDKAT

MANATI

HAMAXI

FIGURE 2. VOLCANOES OF HAWAII RDHETA 90-200



FROM KILAUEA THE NEWEST LAND ON EARTH

FIGURE 3. SAMPLING LOCATIONS RDHETA 90-200

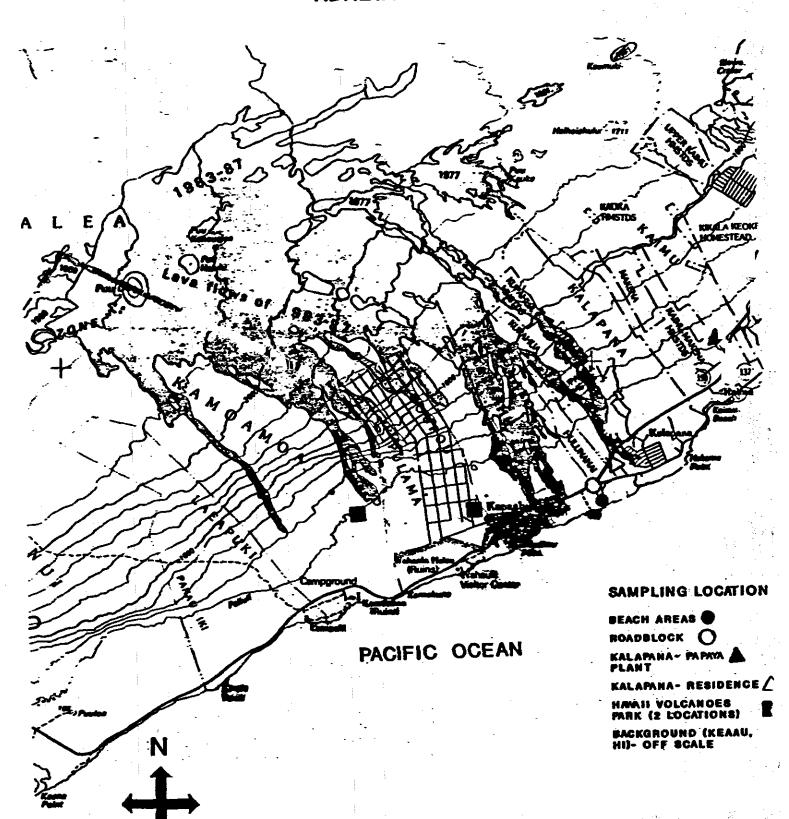


FIGURE 4. CONCENTRATIONS OF HCI IN AIR CONCENTRATION DECAY WITH DISTANCE

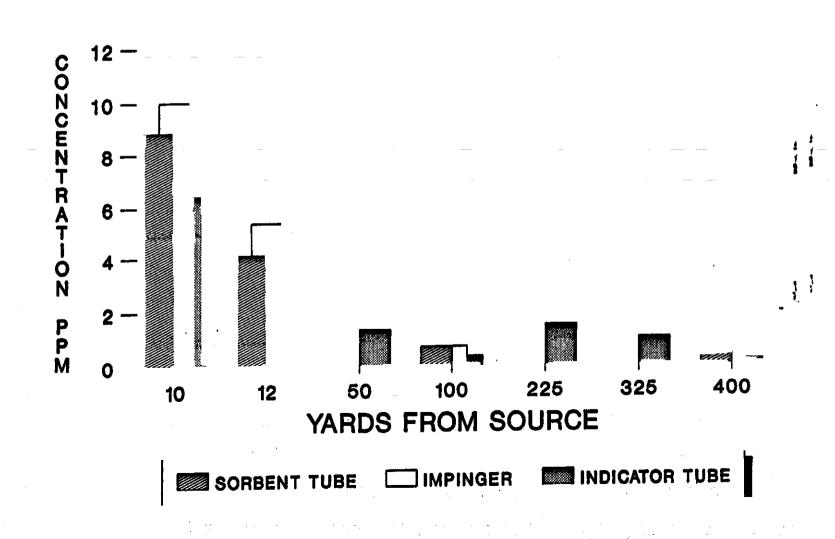


FIGURE 5 PHOTOMICROGRAPH OF GROUND BULK SAMPLE UNDER BRIGHTFIELD ILLUMINATION SHOWING GLASS FRAGMENTS



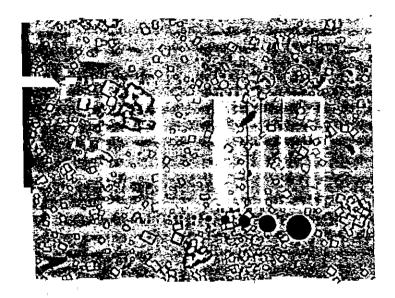
(CIRCLE #2= 10 MICROMETERS)

In addition to this trace metal analysis, the distilled water impinger samples were also analyzed for trace metals to estimate chloride salt content of each sample.

² Pele is described in local Hawaiian religion as the goddess of island volcanoes.

FIGURE 6

PHOTOMICROGRAPH OF AIR SAMPLE UNDER BRIGHTFIELD ILLUMINATION SHOWING CUBIC CRYSTALS



(CIRCLE #7= 10 MICROMETERS)

FIGURE 7

PHOTOMICROGRAPH OF AIR SAMPLE UNDER DIFFERENTIAL INTERFERENCE CONTRAST ILLUMINATION SHOWING GLASS FIBERS



(CIRCLE #7= 10 MICROMETERS)

TABLE 3 HYDROCHLORIC ACID CONCENTRATIONS IN AIR IMPINGER SAMPLING METHODS

RDHETA 90-200

		PROXIMITY TO	HCl - Co	ONCENTRATION IN NAOH	P7M1 H ₂ O	CHLORIDE SALT	AVERAGE CONCENTRATION
LOCATION ⁴	DATE	LAZE PIUNE	TIME (hours)	impinger	infinger	adjustment ²	HCI (PPM)3
BEACH STATION 1	3/13/90	In Plume - 100 yards	2.5	0.74	0.24	0	0.5 (0.25)
BEACH STATION 1	3/14/90	In Plume - 12 yards from source	3,6	5.6	5.3 (4.6)	86.7%	5.4 (4.7)
BEACH STATION 2	3/14/90	In Plume - 10 yards from source	2.3	12	8.1 (7.0)	86.4%	10 (8.6)
ROADBLOCK	3/14/90	Out of Plume	5.6	ND	0.02 (ND)	0	0.01 (0)
KRAAU FIRE STATION	3/14/90	Out of Plume	7.5	0.02	VOID (-)	-	0.02 (-)
ROADBLOCK	3/15/90	Out of Plume	6.7	ND	VOID (-)	-	(-) dN
Kalapana Residence	3/15/90	Out of Plume	7.0	ND	0.06 (ND)	0	0.03 (0)
BEACH STATION 1	3/18/90	In Plume - 100 yards from source	4.3	1.6	0.2 (ND)	0	0.9 (0.7)
BEACH STATION 2	3/18/90	In Plume - 400 yards from source	4.1	0.45	0.42 (0.15)	36%	0.43 (0.15)
HAWAII VOLCANOS PARK	3/18/90	In Plume - 2.5 miles from source	5.8	ND	VOID	-	ND 3
HAWAII VOLCANOS PARK	3/18/90	In Plume - 4.5 miles from source	5,8	VOID	rod	0	100
LIMIT OF QUANTITATION		NaOH IMPINGER	20 mg/sample or				
LIMIT OF DETECTION		H ₂ O impinger Nach H_O	5 mg/sample or a 6 mg/sample or a 2 mg/sample or a	pproximately 0.	01 ppm.		

² mg/sample or approximately 0.04 ppm.

TABLE 3 HYDROCHLORIC ACID CONCENTRATIONS IN AIR IMPINGER SAMPLING METHODS (CONTINUED)

RDHETA 90-200

ppm - Parts per million parts air; ND - Below the limit of detection; LOQ - Detectable concentrations but below the limit of quantitation; NaOH - Sodium Hydroxide impinger media; H₂O - Distilled water impinger media.

- 1 Hydrochloric acid (HCl) Concentrations reported here are based on total chloride ion per sample; adjustment for the chloride believed to be present as salts of sodium, magnesium, and calcium reduced the HCl concentrations as estimated by the concentrations reported in ().
- The chloride selt adjustment is the percent HCl in the air sample after adjustments for chloride selts. This value was calculated based on metals analysis (sodium, magnesium, and calcium) in the impinger samples collected using distilled water media. See appendix 1 for more detail.
- ³ Concentrations of the NaOH impinger and H₂O impinger are averaged for each sampling station. The LOD and LOQ concentrations were used to calculate the average concentrations for sample values below the LOD or between the LOD and LOQ.
- 4 See Methods Section and Figure 4 for more detail on sampling locations.

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TABLE 4 HYDROCHLORIC ACID CONCENTRATIONS IN AIR NIOSH METHOD 7903 - SOLID SORBET TUBE SAMPLES

RDHETA 90-200

			SAMPLING CONCENTRATION IN PPM				
LOCATION	DATE	PROXINITY TO LAZE PLUME	Sampling Time (Hours)	Sample #1	Sample #2	AVERAGE CONCENTRATION IN PPM ³	
BEACH STATION 1	3/13/90	In Plume - 100 yards from source	2.5	1	rod	0.6	
KALAPANA - PAPAYA PLANT	3/13/90	Out of Plume	5.1	ND	NT	D	
BEACH STATION 1	3/14/90	In Plume - 12 yards from source	3.6	5.6	2.6	4.1	
BEACH STATION 2	3/14/90	In Plume - 10 yards from source	2.3	9.1	8.4	8.8	
ROADBLOCK	3/14/90	Out of Plume	5.6	rod	ND	rod	
KEAAU FIRE STATION	3/14/90	Out of Plume	7.5	ND	LOQ	rod	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
ROADBLOCK	3/15/90	Out of Plume	6.7	ND	ND	ИД	\$1
KALAPARA RESIDENCE	3/15/90	Out of Plume	7.0	LOQ	ND	rod	
KALAPANA - PAPAYA PLANT	3/15/90	Out of Plume	7.3	ND	TH	ND	
BEACH STATION 1	3/18/90	In Plume - 100 yards from source	4.3	1.12	0.41	0.76	33
BEACH STATION 2	3/18/90	In Flume - 400 yards from source	4.1	LOQ	0.47	0.35	••
HAWAII VOLCANOS PARKS	3/18/90	In Plume - 2.5 miles from source	5.8	ND	ND	ND	
HAWAII VOLCANOS	3/18/90	In Plume - 4,5 - miles from source	5.8	ND	ND	DM	

TABLE 4 HYDROCHLORIC ACID CONCENTRATIONS IN AIR NIOSH METHOD 7903 - SOLID SORBET TUBE SAMPLES (CONTINUED)

LIMIT OF QUANTITATION (LOQ) LIMIT OF DETECTION (LOD)

21 mg/sample or approximately 0.23 ppm

approximately 0.08 ppm 7 mg/sample

PPM - PARTS PER MILLION PARTS AIR BY VOLUME; NT - SAMPLE WAS NOT TAKEN; ND - BELOW THE DETECTION LIMIT; LOQ - DETECTABLE CONCENTRATION BUT BELOW THE LIMIT OF QUANTIFICATION.

- 1 HC1 CONCENTRATIONS WERE CALCULATED FOR EACH OF TWO SIDE-BY-SIDE SAMPLES ASSUMING ALL CHLORIDE IN EACH SAMPLE WAS PRESENT AS HC1. IT IS THAT SOME OF THE CHLORIDE IN THESE SAMPLES WAS PRESENT AS SALTS OF SODIUM, MAGNESIUM, AND CALCIUM. POSSIBLE
- * SEE METHODS SECTION AND FIGURE 4 FOR MORE DETAIL ON SAMPLING LOCATIONS.
- THE LOQ WAS USED TO CALCULATE THE AVERAGE CONCENTRATIONS FOR VALUES BETWEEN THE LOD AND LOQ.

TABLE 5 SHORT-TERM-INDICATOR TUBE SAMPLING RESULTS1

RDHETA 90-200

SUBSTANCE	SAMPLES		NLOD	CONCENTRATION RANGE (PPM)
Aumonia	3		0	ND
Carbon Dioxide	2		2	400 - 450 ppm
Carbon Disulfide	1		0	ND
Carbon Monoxide	3		0	ND .
Chlorine	2	1	0	ND
Hydrochloric Acid	22	· .	14	ND to 7 ppm
Hydrofluoric Acid	3		0	ND
Hydrogen Sulfide	2		0	ND
Nitrogen Dioxide	2		0	ND
Sulfuric Acid	2		0	ND
Sulfur Dioxide	4		1	ND to 1.5 ppm
				

ppm - Parts per million parts air by volume; NLOD - The number of samples above detectable limits; ND - Below analytical detection limits.

Direct reading sampling results from Beach sampling locations.

TABLE 6 RESPIRABLE DUST CONCENTRATIONS IN AIR1

RDHETA 90-200

LOCATION ²	DATE	PROXIMITY TO LAST PLUME	SAMPLE TIME (hours)	CONCENTRATION (mg/m³)
BEACH STATION 1	3/13/90	In Flume - 100 yards from source	2.5	0.12
BEACH STATION 1	3/14/90	In Plume - 12 yards from source	3.6	0.5
BEACH STATION 2	3/14/90	In Plume - 10 yards from source	2.3	1.3
ROADBLOCK	3/14/90	Out of Plume	5.6	0.03
KEAAU FIRE STATION	3/14/90	Out of Plume	7.5	ND
ROADBLOCK	3/15/90	Out of Plume	6.7	0.03
KALAPANA RESIDENCE	3/15/90	Out of Plume	7	0.01
BEACH STATION 1	3/18/90	In Plume - 100 yards from source	4.3	0.41
BEACH STATION 2	3/18/901	In Plume - 400 yards from source	4.1	0.14
HAWAII VOLCANOS PARK	3/18/90	In Plume - 2.5 miles from source	5.8	0.02
HAWAII VOLCANOS PARK	3/18/90	In Plume - 4.5 miles from source	5.8	0.03

LINIT OF DETECTION FOR RESPIRABLE DUST: 0.01 mg/SAMPLE OR APPROXIMATELY 0.01 mg/m3 FOR A 7.5 HOUR SAMPLE

mg/m3 - MILLIGRAMS PER CUBIC METER OF AIR; ND - BELOW THE LIMIT OF DETECTION.

¹ ALL RESPIRABLE DUST SAMPLES WERE ANALYZED FOR CRYSTALLINE SILICA AND CONCENTRATIONS WERE BELOW DETECTABLE LIMITS: 0.015 mg/sample or approximately 0.03 mg/m³ depending on sample wouldne.

^{*} SEE METHODS SECTION AND FIGURE A FOR MORE DUTAIL ON SAMPLING LOCATIONS

TABLE 7 CONCENTRATIONS OF METALS IN AIR MCE FILTER SAMPLES - NIOSH METHOD 7300 RDHETA 90-200

LOCATION	DATE	PROXINITY TO LAZE PLUME	SAMPLE TIME (hours)	Ca	Cu	CENTRATIONS I	N mg/m³ Mg	Na.		Zn
BEACH STATION 1	3/13/90	In Plume - 100 yards from source	· · · 2.5	ND	ND	ND "	0.01	0.16		ND
BEACH STATION 1	3/14/90	In Plume - 12 yards from source	3.6	ND	0.005	0.005	0.04	0.43		ND
BEACH STATION 2 0.007	3/14/90	In Plume - 10 yards from source	2.3	0.03	ND	ND	0.13	1.0		
ROADBLOCK	3/14/90	Out of Plume	5.6	ND	ND	ND	ND	0.03		ND
KEAAU FIRE STATION	3/14/90	Out of Plume	7.5	ND	ND	ND	ND	0.02		ND
ROADBLOCK	3/15/90	Out of Plume	6.7	ND	ND	ND	ND	ND	Ł	ND
Kalapana Residence	3/15/90	Out of Plume	7.0	ND	ND	ND	ND	ND	1	ND
BEACH STATION 1	3/18/90	In Plume - 100 yards from source	4.3	ND	ND	0,002	0.03	0.27		ND
BEACH STATION 2	3/18/901	In Plume - 400 yards from source	4.1	ND	ND	ND	ND	0.03		MD
HAWAII VOLCANOS PARK	3/18/90	In Plume - 2.5 miles from source	5.8	ND	ND	ND	ND	0.03	ř,	ND
HAWAII VOLCANOS PARK	3/18/90	In Plume - 4.5 miles from source	5.8	ND	ND	ND	ND	ND -	, 3 -	ND
LIMIT OF DETECTION IN LIMIT OF DETECTION IN	mg/SAMPLE A 5-HOUR SAMPLI			0.005 0.008	0.001 0.002	0.001 0.002	0.002 0.003	0.02 0.03	0.0 0.0	

Mg/H3 - MILLIGRAMS PER CUBIC METER OF AIR; ND - BELOW THE LIMIT OF DETECTION; MCE-MIXED CELLULOSE ESTER. METALS: Ca - CALGIUM, Cu - COPPER, Fe - IRON, Mg - MAGNESIUM, Na - SODIUM, Zn - ZINC.

1 SEE METHODS SECTION AND FIGURE 4 FOR MORE DETAIL ON SAMPLING LOCATIONS.

TABLE 8 FIBER CONCENTRATIONS IN AIR1

→ -ROHETA 90-200 -----

LOCATION ³	DATE	PROXIMITY TO LAZE PLUME CON	CENTRATION(f/cc) ²
BEACH STATION 1	3/13/90	In Plume - 100 Yards from Source	(0.004)*
BEACH STATION 1	3/14/90	In Plume - 12 Yards from Source	(0.01)*
BEACH STATION 2	3/14/90	In Plume - 10 Yards from Source	0.16
ROADBLOCK	3/14/90	Out of Plume	ND
KEAAU FIRE STATION	3/14/90	Out of Plume	ND
ROADBLOCK	3/15/90	Out of Plume	ND
KALAPANA RESIDENCE	3/15/90	Out of Plume	ND
BEACH STATION 1	3/18/90	In Plume - 100 Yards from Source	(0.01)*
BEACH STATION 2	3/18/90	In Plume - 400 Yards from Source	ND
HAWAII VOLCANOS PARK	3/18/90	In Plume - 2.5 Miles from Source	ND
HAWAII VOLCANOS PARK	3/18/90	In Plume - 4.5 Miles from Source	ND

f/cc - Pibers per cubic centimeter of air; ND - samples below analytical detection limits.

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Samples were analyzed using transmission electron microscopy, NIOSH Method 7402

² Due to low concentrations of fibers in some of the samples, air concentrations reported are considered approximate.

³ See Methods Section and Figure 4 for more detail on sampling locations.

HC1 CONCENTRATION ADJUSTMENTS FOR CHLORIDE SALT INTERFERENCE

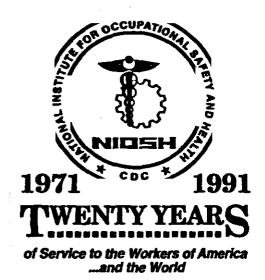
The dissolved solids in seawater are comprised largely of chloride salts as indicated in the table below. (23)

DISSOLVED SOLIDS IN SEAWATER AS SALTS

SALT	PARTS PER THOUSAND (%)	WEIGHT (%)
SODIUM CHLORIDE, NaCl	23.477	68.085
MAGNESIUM CHLORIDE, MgCl2	4.981	14,445
SODIUM SULFATE, Na2SO4	3.917	11.359
CALCIUM CHLORIDE, CaCl,	1.102	3.196
POTASSIUM CHLORIDE, KC1	0.664	1.926
SODIUM BICARBONATE, NaHCO,	0.192	0.557
POTASSIUM BROMIDE, KBr	0.096	0.278
BORIC ACID, H ₃ BO ₃	0.026	0.075
STRONTIUM CHLORIDE STC1,	. 0.024	0.070
SODIUM FLUORIDE, NaF	0.003	0.009
TOTALS	34.482	100.000

Impinger and sorbent tube air samples taken during this survey to quantify HCl concentrations were analyzed for the presence of the chloride anion (Cl⁻) using ion chromatography according to NIOSH Method 7903⁽⁴⁾ The ion chromatograph cannot distinguish chloride anion derived from HCl from the chloride present as ocean salts. Consequently, the presence of chloride salts in air presents a potential source of analytical interference that could reduce HCl concentrations from those values calculated using total chloride. To address this potential bias, each distilled water impinger sample was snalyzed for the metals commonly bound with chlorine in ocean salts (sodium, magnesium, and calcium). The number of moles of chloride that could be consumed by each of these metals was subtracted from total chloride anion for each sample. The adjusted chloride content of each impinger sample was then used to calculate HCl concentrations with adjustment for chloride salts. Estimates of the salt adjusted HCl concentration are reported in Table 3 of this report.

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Airborne fibers also were detected in samples collected from the LAZE plume. Table 8 presents fiber concentrations in air samples analyzed by TEM; these concentrations ranged from ND to 0.16 f/cc. Airborne fibers were only detected in the samples collected from the beach sampling stations. Three of the 4 samples with detectable fiber concentrations had low fiber densities on the filters and the reported concentrations, 0.004 to 0.01 f/cc, should be considered approximate. Energy dispersive x-ray analysis suggests a large portion of these fibers were comprised of calcium and sulfur with a morphology characteristic of gypsum; although, the calcium to sulfur ratios were variable and exact fiber identity (as gypsum) could not be verified in all instances. Some of the airborne fibers appeared to be comprised largely of calcium. Glass fibers were also detected on some of the air samples. Figure 7 is a photomicrograph of an air sample observed under differential interference contrast illumination showing some of these isotropic fibers. Gypsum and fibrous glass particles could cause irritation to the eyes, skin, and upper respiratory tract.

There are no occupational exposure standards specifically for gypsum fibers or glass particles; although the OSHA standard for total gypsum dust is 15 mg/m³ as a TWA. NIOSH and ACGIH recommend gypsum exposure be maintained below 10 mg/m³ as a TWA. Exposures to gypsum dusts (including gypsum fibers) were well below these exposure standards. Airborne fiber concentrations were also low by comparison to existing occupational exposure standards/criteria for fibrous glass. NIOSH recommends a TWA exposure limit of 3 f/cc for glass fibers \leq 3.5 um in diameter and \leq 10 um in length. ACGIH recommends a TLV limit of 10 mg/m³ for fibrous glass as a TWA exposure. Concentrations of airborne fibers (including fibrous glass) were below these occupational criteria.

VII. CONCLUSIONS

1. The interaction of lava and sea water generated quantifiable concentrations of HCl and HF; HCl was predominate with lesser amounts of HF. Condensate samples of LAZE were highly acidic with a pH of 1.3. These findings are consistent with research efforts of the U.S. Geological Survey indicating HCl can be formed by the steam hydrolysis of magnesium chloride salts precipitated when sea water is evaporated by lava. (21,22)

Potential for exposure to inorganic acids (HCl and HF) presents the most significant health risk from LAZE. HCl concentrations were highest in dense plumes of LAZE within approximately 12 yards of the sea. The HCl concentrations measured at those sampling locations exceeded the 5 ppm ceiling standard and presented an occupational health hazard according to occupational exposure criteria of OSHA, ACGIH, and NIOSH. HF concentrations were below existing occupational exposure standards; although, HF would produce additive exposure effects in combination with HCl.

HCl and HF concentrations decreased with distance from the source. At distances of approximately 400 yards or greater, HCl concentrations, directly in the diluted plume, were less than 1 ppm.

- 2. Sulfur dioxide (SO_2) was detected in one of four short-term detector—tube samples at a concentration of approximately 1.5 ppm. This short—term, area sample was high in comparison to the NIOSH-REL for SO_2 (0.5—ppm as a TWA) and the EPA primary and secondary ambient Air Quality—Standards (pg. 17). This demonstrates the potential for intermittent or periodic SO_2 exposure near areas of volcanic activity and active lava—flow.
- 3. Short-term, detector tube samples collected in the LAZE plume were below detectable limits for: ammonia, carbon disulfide, carbon monoxide, chlorine, hydrofluoric acid, hydrogen sulfide, nitrogen dioxide, and sulfuric acid.
- 4. The LAZE did not contain detectable concentrations of organic gases.
- 5. Crystalline silica concentrations in TWA air samples were below detectable limits, (less than approximately 0.03 mg/m³). This is consistent with the basaltic nature of Hawaiian lavas. (1.3)
- 6. Airborne particulates in the LAZE plume were comprised largely of sodium chloride crystals. Airborne fibers were detected at quantifiable concentrations in one of 5 samples collected from the beach sampling stations; the fiber concentration was 0.16 f/cc. These fibers were comprised largely of hydrated calcium sulfate similar to the mineral gypsum. Glass fibers were also detected in some samples collected from beach sampling stations. These fiber concentrations did not exceed the occupational exposure criteria of OSHA, ACGIH, or NIOSH for gypsum or fibrous glass.

- 1. Individuals should avoid exposure to the concentrated lava/sea water aerosol near its origin to prevent overexposure to acid gases, specifically HCl.
- 2. Worker exposure to HCl should be maintained below a ceiling value of 5 ppm; this will likely control any HF exposure and the potential for additive health effects. Appropriate personal protective gear (including a chemical cartridge respirator for acid gases and eye goggles or a full facepiece chemical cartridge respirator) is recommended in instances when exposure to the lava/sea water aerosol, near its origin, is unavoidable. A respirator should be selected for each worker to provide a good fit or seal; a proper fit can not be obtained if there is facial hair in the seal area. These respirators should be used as a part of a formal respiratory protection program including standard operating procedures for respirator use, training, fit testing, maintenance, and storage. The program should comply with the OSHA General Industry Occupational Safety and Health Standards, 29 CFR 1910.134.
- 3. All individuals in the areas near lava/sea water interaction should be informed about potential exposures to acid gases (HCI):
 - Area workers (park or civil defense employees, etc.) should be informed about the
 potential for acid gas exposure near the ocean and instructed on the potential health
 risks.

 Warning signs should be posted along nearby roads and at blockades to alert visitors to the area about the potential for exposure to acid gases. For example:

CAUTION MIST FROM LAVA AND SEA WATER INTERACTION CONTAINS HYDROCHLORIC ACID AND MAY CAUSE RESPIRATORY SYMPTOMS. YOUNG CHILDREN, THE ELDERLY, OR INDIVIDUALS WITH CARDIOPULMONARY CONDITIONS MAY BE AT INCREASED RISK AVOID CONTACT WITH THIS MIST

- Written warning should be given to all residents living in the areas near the lava/sea water interaction. This warning should provide health effects information and emphasize the increase exposure risk for young children, the elderly or individuals with cardiopulmonary problems.
- Prudent public health education on the potential health hazards from lava/sea water interaction should be provided for area residents, workers, and visitors on a scheduled basis.
- 4. A warning siren, or other appropriate warning device, may be appropriate to alert area residents when the lava/sea water aerosol is directed towards nearby villages by prevailing winds. This would allow some early notice for those individuals at increased exposure risk.
- 5. Short-term indicator tubes could be used by local health or civil defense personnel as a rapid method to assess potential exposure to HCl, HF, or SO₂. The indicator tube samples for HCl were in good agreement with HCl measurements taken during this survey by the other sampling methods. Samples should be taken to assess HCl and HF

concentrations when the lava/sea water aerosol is directed towards populated areas.

- Additional environmental sampling is also recommended to better define LAZE characteristics and exposure hazards under varying conditions of lava flow and wind patterns.
- 7. The occupational exposure criteria referenced in this report are derived from occupational health research settings and are not an appropriate tool for evaluating community health risks. There are no community health standards to evaluate HCl exposure risks for the general population. Community exposures to HCl certainly should not exceed the 5 ppm ceiling standard used for occupational settings; a lower exposure limit may be appropriate to protect public health and welfare.

IX. REFERENCES

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X. <u>AUTHORSHIP AND ACKNOWLEDGEMENT</u>

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TABLE 3 HYDROCHLORIC ACID CONCENTRATIONS IN AIR IMPINGER SAMPLING METHODS

RDHETA 90-200

AVERAGE	HC	- CONCENTRATION IN	PPM ¹	CHLO	RIDE
PR CONCENTRATION	OXIMITY TO	SAMPLING NaOH		H ₂ O	SALT
LOCATION ⁴ IMPINGER IMPINGER	DATE	LAZE PIUME STMENT ² HCI (F	PPM) ³	TIME (hours)	
BEACH STATION 1 0.24	3/13/90 0	In Plume - 100 yards 0.5 (0.25	5)	2.5	0.74
BEACH STATION 1 5.3 (4.6)	3/14/90 86.7%	In Plume - 12 yards 5.4 (4.7) from source		3.6	5.6
BEACH STATION 2 8.1 (7.0)	3/14/90 86.4%	In Plume - 10 yards 10 (8.6) from source		2.3	12
ROADBLOCK 0.02 (ND)	3/14/90 0	Out of Plume 0.01 (0)	5.6	ND	
KEAAU FIRE STATION VOID (-)	3/14/90 -	Out of Plume 0.02 (-)	7.5	0.02	
ROADBLOCK VOID (-)	3/15/90 -	Out of Plume ND (-)	6.7	ND	
KALAPANA RESIDENCE 0.06 (ND)	3/15/90 0	Out of Plume 0.03 (0)	7.0	ND	
BEACH STATION 1 0.2 (ND)	3/18/90 0	In Plume - 100 yards 0.9 (0.7) from source		4.3	1.6
BEACH STATION 2 0.42 (0.15)	3/18/90 36%	In Plume - 400 yards 0.43 (0.15) from source	4.1	0.45	
HAWAII VOLCANOS	3/18/90	In Plume -		5.8	ND
VOID PARK	-	ND 2.5 miles from source			
HAWAII VOLCANOS	3/18/90	In Plume -		5.8	
VOID LO	Q	0 LOQ 4.5 miles from source			
LIMIT OF QUANTITATION		NaOH IMPINGER		20 mg/sar	nple or
approximately 0.04 ppm.		H₂O IMPINGER		5 mg/sample of	or
approximately 0.01 ppm. LIMIT OF DETECTION		NaOH		6 mg/sample of	or
approximately 0.01 ppm. approximately 0.04 ppm.		H ₂ O		2 mg/sample of	or

TABLE 3 HYDROCHLORIC ACID CONCENTRATIONS IN AIR IMPINGER SAMPLING METHODS (CONTINUED)

RDHETA 90-200

ppm - Parts per million parts air; ND - Below the limit of detection; LOQ - Detectable concentrations but below the limit of quantitation; NaOH - Sodium Hydroxide impinger media; H_2O - Distilled water impinger media.

- ¹ Hydrochloric acid (HCl) Concentrations reported here are based on total chloride ion per sample; adjustment for the chloride believed to be present as salts of sodium, magnesium, and calcium reduced the HCl concentrations as estimated by the concentrations reported in ().
- ² The chloride salt adjustment is the percent HCl in the air sample after adjustments for chloride salts. This value was calculated based on metals analysis (sodium, magnesium, and calcium) in the impinger samples collected using distilled water media. See appendix 1 for more detail.
- 3 Concentrations of the NaOH impinger and $\rm H_2O$ impinger are averaged for each sampling station. The LOD and LOQ concentrations were used to calculate the average concentrations for sample values below the LOD or between the LOD and LOQ.
- ⁴ See Methods Section and Figure 4 for more detail on sampling locations.

TABLE 4 HYDROCHLORIC ACID CONCENTRATIONS IN AIR NIOSH METHOD 7903 - SOLID SORBET TUBE SAMPLES

RDHETA 90-200

LOCATION	SAMPLE	DATE SAMPLE		MPLING CONCENTRATION IN PROXIMITY TO AGE CONCENTRATION	IN PPM SAMPLING
#1	#2	OAWII EE	IN PPM ³	LAZE PLUME	TIME (HOURS)
BEACH STATI		3/13/90	0.0	In Plume - 100 yards	2.5
1	LOQ		0.6	from source	
KALAPANA - PAPAYA		3/13/90		Out of Plume	5.1
PLANT		ND		NT	ND
BEACH STATION 1		3/14/90 5.6		In Plume - 12 yards 2.6 from source	3.6 4.1
BEACH STATION 2		3/14/90 9.1		In Plume - 10 yards 8.4 from source	2.3 8.8
ROADBLOCK		3/14/90 LOQ		Out of Plume ND	5.6 LOQ
KEAAU FIRE STATION		3/14/90 ND		Out of Plume LOQ	7.5 LOQ
ROADBLOCK		3/15/90 ND		Out of Plume ND	6.7 ND
KALAPANA RESIDENCE		3/15/90 LOQ		Out of Plume ND	7.0 LOQ
KALAPANA - PAPAYA PLANT		3/15/90 ND		Out of Plume NT	7.3 ND
BEACH STATION 1		3/18/90 1.12		In Plume - 100 yards 0.41 from source	4.3 0.76
BEACH STATION 2		3/18/90 LOQ		In Plume - 400 yards 0.47 from source	4.1 0.35
HAWAII VOLCANOS PARKS		3/18/90 ND		In Plume -	5.8
				ND 2.5 miles from source	ND
HAWAII VOLCANOS		3/18/90		In Plume -	5.8
PARK		ND		ND 4.5 - miles from source	ND

TABLE 4 HYDROCHLORIC ACID CONCENTRATIONS IN AIR NIOSH METHOD 7903 - SOLID SORBET TUBE SAMPLES (CONTINUED)

RDHETA 90-200

LIMIT OF QUANTITATION (LOQ)		21 mg/sample or approximately 0.23 ppm
LIMIT OF DETECTION (LOD) 7 mg/sample	or	approximately 0.08 ppm

PPM - PARTS PER MILLION PARTS AIR BY VOLUME; NT - SAMPLE WAS NOT TAKEN; ND - BELOW THE DETECTION LIMIT; LOQ - DETECTABLE CONCENTRATION BUT BELOW THE LIMIT OF QUANTIFICATION.

¹ HCI CONCENTRATIONS WERE CALCULATED FOR EACH OF TWO SIDE-BY-SIDE SAMPLES ASSUMING ALL CHLORIDE IN EACH SAMPLE WAS PRESENT AS HCI. IT IS POSSIBLE THAT SOME OF THE CHLORIDE IN THESE SAMPLES WAS PRESENT AS SALTS OF SODIUM, MAGNESIUM, AND CALCIUM.

 $^{^{2}\,}$ SEE METHODS SECTION AND FIGURE 4 FOR MORE DETAIL ON SAMPLING LOCATIONS.

 $^{^{\}rm 3}\,$ THE LOQ WAS USED TO CALCULATE THE AVERAGE CONCENTRATIONS FOR VALUES BETWEEN THE LOD AND LOQ.

TABLE 5 SHORT-TERM INDICATOR TUBE SAMPLING RESULTS¹ RDHETA 90-200

SUBSTANCE	SAMPLES	NLOD	CONCENTRATION RANGE (PPM)
Ammonia	3	0	ND
Carbon Dioxide	2	2	400 - 450 ppm
Carbon Disulfide	1	0	ND
Carbon Monoxide	3	0	ND
Chlorine	2	0	ND
Hydrochloric Acid	22	14	ND to 7 ppm
Hydrofluoric Acid	3	0	ND
Hydrogen Sulfide	2	0	ND
Nitrogen Dioxide	2	0	ND
Sulfuric Acid	2	0	ND
Sulfur Dioxide	4	1	ND to 1.5 ppm

 \mbox{ppm} - Parts per million parts air by volume; NLOD - The number of samples above detectable limits; ND - Below analytical detection limits.

¹Direct reading sampling results from Beach sampling locations.